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Hydrotreating of diluted Maya crude with NiMo/Al_2O_3-TiO_2 catalysts: effect of diluent composition

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Abstract

This work analyzes the changes in hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeasphaltenization (HDAs) and hydrodemetallization (HDM) activities, when a NiMo/TiO_2/Al_2O_3-catalyst is evaluated under three different feedstocks containing heavy Maya petroleum, i.e., Maya-diesel (M-D), hydrodemetallized Maya-diesel (HM-D) and hydrodemetallized Maya-naphtha (HM-N). A NiMo/Al_2O_3 catalyst was also tested using HM-N as feed, in order to enquire on the effect of changing the nature of the support from Al_2O_3 to TiO_2/Al_2O_3. The results show that the choice of diluent when performing catalytic activity tests for the ranking of catalyst formulations for hydrotreatment of heavy petroleum like Maya is critical. The incorporation of Ti to the support of the conventional NiMo/Al_2O_3 catalyst improves the functionalities of the catalyst (HDS, HDN, HDAs), possibly due to Ti-enhanced hydrogenating and hydrodesulfurization functions. The number of coordinatively unsaturated sites (CUS) on the surface of the sulfided phase was higher in the Ti-containing catalyst.
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Keywords: Hydrotreatment; Maya petroleum; NiMo/TiO_2-Al_2O_3 catalyst; Diluent effect

1. Introduction

The procedures for the evaluation of catalytic activity are of great importance when searching for the best catalyst to be used in an industrial installation. In the particular case of hydrotreating catalysts, the more stringent environmental regulations concerning specially the sulfur compounds emissions has motivated a large effort in the design of new more active catalyst formulations. Because of this, the methodology for the screening of new hydrotreating catalysts formulations has recently received attention. In the early stages of catalyst screening the experiments are usually performed using model molecules as feed. However, the model molecule should be chosen according to the composition of the real feedstock with which the catalyst will be faced. It is well known that the ranking of different catalyst formulations will depend to a great extent on the model feed used in the catalytic activity study. Clearly, the catalyst performance is not the same if one uses as feed thiophene, a molecule easy to desulfurize, or 4,6 dimethyldibenzothiophene, a very refractory molecule, which can desulfurize through several reaction routes. In the past, the investigations that have dealt with the problem of comparing the activity of different catalysts using different model molecules have led to conflicting results. In one study, the ranking of NiMo and CoMo/Al_2O_3 catalysts with thiophene or DBT was found to be the same [1]. Other authors have found that the ranking of HDS catalysts, containing or not Ti in the support, using model molecules, thiophene and DBT, and a real feed, gasoil, is the same [2]. In all cases these authors found a beneficial effect of incorporating titanium to the support. However, in other work, Bacaud et al. [3] did not arrive at the same conclusion and find that the positive effect of Ti in HDS of DBT is not confirmed when using diesel as feed. Other works have also pointed out differences in results when comparing gas versus liquid phase feeds in HDS of DBT [4,5]. Therefore, the problem of selecting an appropriate feed for the activity tests becomes even greater at the final stages of the development of catalyst formulation,

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when the catalytic tests in microplant have to be made with a mixture feed as close as possible to the industrial feedstock.

The selection of catalysts for the hydrotreatment of heavy petroleum fractions or heavy petroleum has some additional difficulties for the experimentation at microplant level. Some of them are related to the high viscosity of the feed and to the high content of metals (Ni and V) and asphaltenes. To solve the viscosity problem during catalytic evaluation, the experiments are normally performed with a diluted model feed, which usually consists of the real feed diluted with lighter distillates, such as diesel or naphtha.

Today, when heavier petroleum like the Mexican heavy Maya has to be processed, it is important to develop adequate methodologies for catalyst testing and screening. In the particular case of hydrotreatment of heavy Maya petroleum, for the catalytic tests in microplant it is necessary to use a diluted feed in order to minimize the experimental problems generated by its high viscosity. However, the effect of the solvent can change considerably the performance of the catalyst. It is obvious that the ratio of vapor to liquid phase will change substantially depending on the type and amount of solvent used. The degree of evaporation of the solvent at the conditions of the reaction will alter the reactant concentrations in the liquid and vapor phases as well as the wetting of the catalyst. Some results on the effect of the solvent have been published for the HDS of model molecules like DBT [6], or for real feeds [7]. In this latter case the "matrix effect" observed during the hydrodesulfurization of diesel oil, was explained as the result of competitive adsorption of aromatic compounds, which caused a partial blockage of the active surface. Recently, an effort to identify the origin of the discrepancies observed between gas and liquid phase hydrotreatment reactions and to explain the influence of "inert" solvents upon the observed reaction rate was made using the hydrogenation of tetraline as model reaction in the presence of paraffins of different molecular weight used as solvents. In this study, care was taken to avoid diffusional limitations and the inhibiting effect of H_2S. It was concluded that the observed drop in catalyst activity was due to a competitive effect between the reactant and solvent molecules for the adsorption on the catalyst surface [8]. Clearly, if the problem is difficult in the study of model reactions, which are made under controlled conditions, such as absence of diffusional intrusions, control of the rate of evaporation, control of the effect of H_2S inhibition, controlled concentration and type of aromatics present, etc., the effects present during the evaluation of real feeds are much more difficult to analyze.

Therefore, for the ranking of catalyst formulations for the hydrotreatment of heavy feeds it is important to select adequately not only the type of solvent but also the relative proportion in which it is used. In our particular case, since the high metal content of the Maya petroleum can cause a partial deactivation of the catalyst, it is also important to establish the effect that on the catalyst activity has a previous demetallization of the feedstock. In spite of its importance, this problem has not been properly addressed in the open literature. It is the object of the present work to analyze the changes in hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeasphaltenization (HDAs) and hydrodemetallization (HDM) activities, when a NiMo/Al_2O_3-TiO_2 catalyst is evaluated under three different feedstocks containing heavy Maya petroleum, i.e., Maya-diesel (M-D), hydrodemetallized Maya-diesel (HM-D) and hydrodemetallized Maya-naphtha (HM-N). A NiMo/Al_2O_3 catalyst was also tested using HM-N as feed, in order to enquire on the effect of changing the nature of the support from Al_2O_3 to TiO_2/Al_2O_3.

2. Experimental

The NiMo/TiO_2/Al_2O_3 and NiMo/Al_2O_3 catalysts used in the catalytic tests contain 10 wt.% Mo and 2.5 wt.% Ni. The amount of Ti in the support of the NiMo/TiO_2/Al_2O_3-catalyst was 5 wt.%. The TiO_2/Al_2O_3 support was prepared by pore volume impregnation of cylindrical extrudates of γ-Al_2O_3, obtained from calcination of boehmite Versal-450 at 550 °C, with a solution containing the adequate amount of titanium isopropoxide in *n*-propanol. After impregnation of Ti the support was dried (100 °C, 4 h) and calcined (550 °C, 4 h). The NiMo catalysts were prepared by impregnating either Al_2O_3 or Al_2O_3-TiO_2 by pore volume with an aqueous solution containing the precursor salts of Ni and Mo. The impregnating solution was prepared by dissolving MoO_3 and $Ni(NO_3)_2$ in a NH_4OH aqueous solution (pH = 9.0). The catalysts were subsequently dried (100 °C, 4 h) and calcined (450 °C, 4 h). Before the catalytic tests the catalysts were sulfided at 28 kg/cm^2 under a two level temperature program, 260 °C (3 h) and 320 °C (5 h), using a H_2/HC ratio of 2000 ft^3/bbl and 20 ml/h of straight-run gas oil (1.7 wt.% S) contaminated with 1 wt.% of dimethyldisulfide, corresponding to an LHSV of 2.0 h^{-1}.

The reaction experiments were conducted in a continuous flow microplant unit equipped with a 0.5 in. diameter tubular reactor to which 7.4 g of catalyst were loaded. The timeonstream of each catalytic test was 60 h. Three different mixtures were used as feedstock in the reaction experiments: (i) hydrodemetallized Maya-naphtha (32/68 wt.%), HM-N, (ii) hydrodemetallized Maya-diesel (50/50 wt.%), HM-D, and (iii) Maya-diesel (50/50 wt.%), M-D.

Total sulfur and nitrogen were determined with an Antek analyzer. The asphaltene content was determined as the amount of compounds insoluble in n-pentane. The analysis of metals, Ni and V, was performed with a Perkin-Elmer 2380 atomic absorption spectrophotometer. The textural properties of supports and catalysts were evaluated in a Quantachrome Nova 2000 nitrogen physisorption apparatus. The XRD determinations were performed in a Siemens D-500 using Cu Kα radiation (λ = 1.5409 Å). The Raman experiments were performed in a Nicolet FT-Raman 950 spectrometer at room temperature with a resolution of 2 cm^{-1}.

The dynamic adsorption of NO over the sulfided catalysts was performed at 2 °C in a Micromeritics Pulse Chemisorb apparatus using helium as carrier gas. Before NO adsorption, the catalysts were sulfided in the same cell using a flow of 20 ml/min of H_2S (15 vol.%)/H_2 during 4 h at 400 °C. Pulses of 1.68 mol of NO were injected until saturation of the sample.

The carbon content in the used catalysts was determined after reaction in a Leco SC-444 carbon and sulfur analyzer.

3. Results and discussion

The main properties of the different feed stocks are given in Table 1. Clearly, sulfur and nitrogen content in the different feed stocks increase following the sequence HM-N < HM-D < M-D. Comparing the content of contaminants for HM-D and M-D indicates that previous hydrotreatment of the feed with a hydrodemetallization catalyst reduces nitrogen (61%), sulfur (28%), asphaltenes (24%) and metals (Ni, 50%; V, 66%) significantly, making the HM-D feed much more light than M-D.

The composition and textural characterization of supports and catalysts are presented in Table 2. Concerning the $TiO_2(5)/Al_2O_3$ support, the incorporation of Ti causes a small decrease in the surface area of the alumina (~5%), and in the pore volume (~8%), indicating a good distribution of Ti on the surface. The pore size distribution indicated that as a result of Ti incorporation, some of the smaller pores were lost while some wider pores were created, shifting slightly the pore volume. The deposition of Mo and Ni on the support surface caused a greater drop in the surface area and pore volume and a small decrease in the average pore diameter (APD). These results suggest that although some pore blockage occurs, the Mo and Ni phases are deposited on the walls of the pores. Hence the incorporation of Ti changes a little the textural properties of alumina and it appears that the Ni and Mo phases are well dispersed.

Table 2
Composition and textural characterization of supports and catalysts

	Support		Catalyst	
	Al_2O_3	$TiO_2(5)/Al_2O_3$	$NiMo/Al_2O_3$	$NiMo/TiO_2(5)/Al_2O_3$
SA (m^2/g)	241	228	209	186
PV (cm^3/g)	0.50	0.46	0.39	0.32
APD (Å)	60.5	60.7	59	56
PVD (vol.%)				
<50 Å	15.28	17.28	17.5	21.16
50–100 Å	60.61	54.93	59.9	55.27
100–250 Å	16.70	18.49	15.2	16.53
250–500 Å	5.60	6.08	5.8	5.50
>500 Å	1.82	3.22	2.5	1.53
Mo (wt.%)			12.2	11.62
Ni (wt.%)			2.7	2.46
Ti (wt.%)		5.0		4.7

PV: average pore volume; APD: average pore diameter; PVD: pore volume distribution; SA: surface specific area.

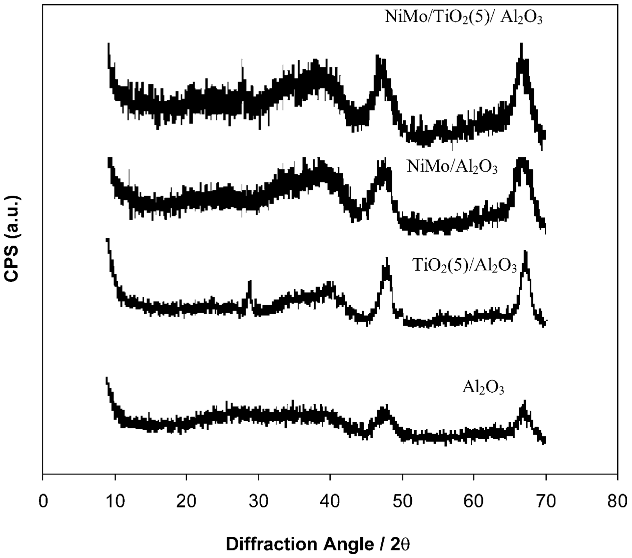

Fig. 1. XRD patterns of supports and catalysts.

Fig. 1 displays the XRD patterns of the supports and catalysts. Both supports, Al_2O_3 and $TiO_2(5)/Al_2O_3$, showed some of the typical reflections of poorly crystallized γ-alumina. However, the $TiO_2(5)/Al_2O_3$ sample showed a small additional peak corresponding to the main reflection of TiO_2-anatase, (1 0 1), suggesting the formation of some small TiO_2 particles on the alumina surface. The existence of TiO_2 particles on the surface of $TiO_2(5)/Al_2O_3$ was also confirmed by the Raman spectroscopy results (not shown

Table 1
Composition of feedstocks

	M	HM	Diesel	Naphtha	Feed (wt.%)		
					HM-N (32/68)	HM-D (50/50)	M-D (50/50)
Density (20/4 °C)	0.9251	0.8940	0.8267	0.7489	0.8401	0.8505	0.8736
Nitrogen (wt.%)	0.3	0.2560	0.0147		0.0873	0.1325	0.1837
Sulfur (wt.%)	3.52	1.645	0.037	<5.0 wppm	0.437	0.841	2.211
Asphaltene (wt.%, *n*-C5 insol.)	12.7	7.87			4.35	6.36	8.43
Ni (wppm)	57.50	46.40			14.93	25.04	25.22
V (wppm)	256.71	143.24			61.59	86.84	129.11
Ni + V (wppm)	314.21	189.64		48.97	76.52	111.88	164.32

HM-N: hydrodemetallized Maya + naphtha; HM-D: hydrodemetallized Maya + diesel; M-D: Maya + diesel.

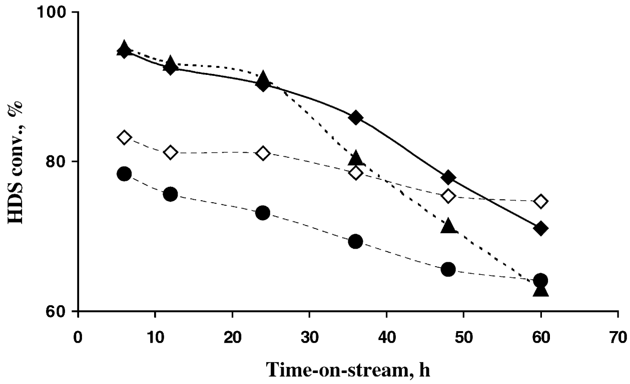

Fig. 2. HDS conversion vs. time-on-stream for (▲) $NiMo/Al_2O_3$ with HM-N feed, (◆) $NiMo/TiO_2(5)/Al_2O_3$ with HM-N feed, (◇) $NiMo/TiO_2(5)/Al_2O_3$ with HM-D, (●) $NiMo/TiO_2(5)/Al_2O_3$ with M-D feed.

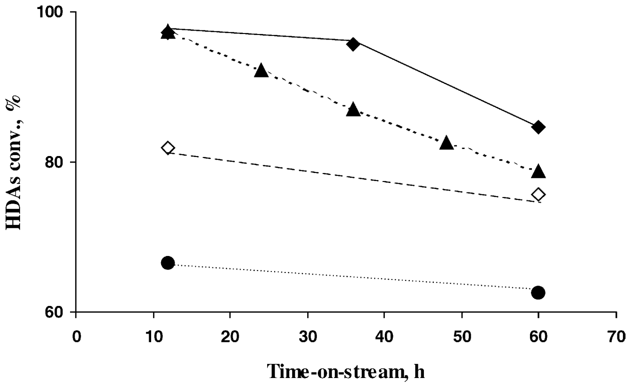

Fig. 4. HDAs conversion vs. time-on-stream for (▲) $NiMo/Al_2O_3$ with HM-N feed, (◆) $NiMo/TiO_2(5)/Al_2O_3$ with HM-N feed, (◇) $NiMo/TiO_2(5)/Al_2O_3$ with HM-D feed, (●) $NiMo/TiO_2(5)/Al_2O_3$ with M-D feed.

here), which showed the presence of the characteristic Raman peaks of anatase at 144, 399, 520 and 643 cm^{-1}.

The diffractograms of the $NiMo/Al_2O_3$ and $NiMo/TiO_2(5)/Al_2O_3$ catalysts showed only reflections corresponding to γ-Al_2O_3, suggesting a good dispersion of the Ni and Mo oxide phases.

The results from the HDS, HDN, HDAs and HDM activity tests with the catalysts using the three different feeds are shown in Figs. 2–5, respectively. To assess the effect of incorporating Ti to the catalyst support, in the same figures the evaluation of the $NiMo/Al_2O_3$ catalyst is included.

The hydrodesulfurization results in Fig. 2 indicate that the change of feedstock produces important changes in activity. Changing the feedstock from HM-N to M-D can lead to differences in conversion from 71.08 to 64.09% after 60 h time-on-stream. Comparison of the activities obtained with HM-D and M-D indicate that a previous hydrodemetallization of the feed, which consists in the partial elimination of Ni and V from the feed, causes an increase in catalyst activity. In general it is observed as expected that the heavier the feed, the lower the catalyst activity. Thus, higher initial activities were obtained with HM-N, followed by HM-D and by M-D. The sole change of solvent from naphtha to diesel causes a 10% decrease in the initial catalyst activity. This change can be due in part to the difference in relative proportions of solvent to Maya petroleum, but also to the change in the composition of the solvent. Figs. 2–5 show that the stability of the catalysts is not the same with the different feed stocks, consequently the initial activity trend HM-N > HM-D > M-D, changed after 60 h time-on-stream to the sequence HM-D > HM-N > M-D. It appears that the catalyst losses activity at a greater rate when naphtha is used as solvent for hydrotreated Maya. In this case the catalyst shows a steeper downward slope in the conversion versus time-on-stream curve. This higher rate of catalyst poisoning with the lighter feedstock was not expected and is clearly the result of a process different from the normal carbon deposition that occurs during the operation of HDT catalysts. In fact the heavier feeds, which contain greater concentrations of carbon precursors, are normally expected to cause a faster deactivation rate.

Concerning the effect of incorporating Ti to the support, it is observed that although the initial HDS activity is similar

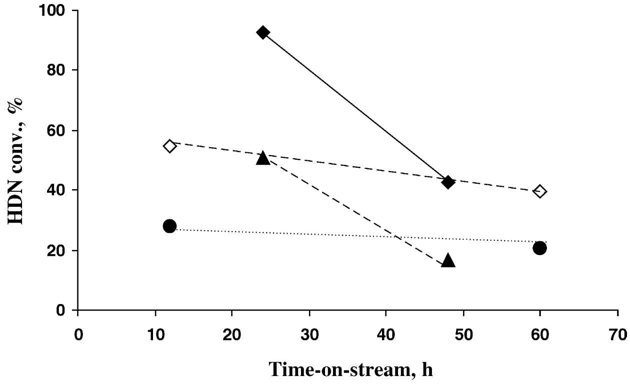

Fig. 3. HDN conversion vs. time-on-stream for (▲) $NiMo/Al_2O_3$ with HM-N feed, (◆) $NiMo/TiO_2(5)/Al_2O_3$ with HM-N feed, (◇) $NiMo/TiO_2(5)/Al_2O_3$ with HM-D feed, (●) $NiMo/TiO_2(5)/Al_2O_3$ with M-D feed.

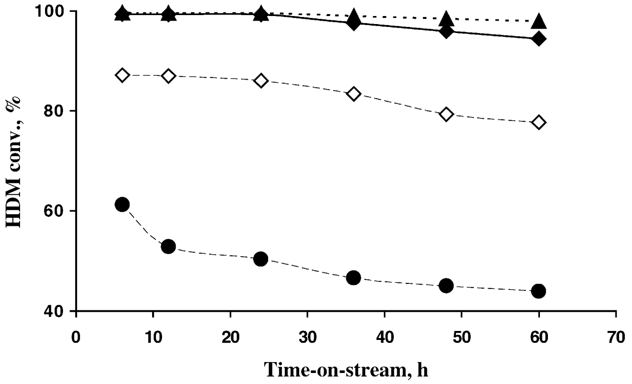

Fig. 5. HDM conversion vs. time-on-stream for (▲) $NiMo/Al_2O_3$ with HM-N feed, (◆) $NiMo/TiO_2(5)/Al_2O_3$ with HM-N feed, (◇) $NiMo/TiO_2(5)/Al_2O_3$ with HM-D feed, (●) $NiMo/TiO_2(5)/Al_2O_3$ with M-D feed.

for the $NiMo/Al_2O_3$ and $NiMo/TiO_2(5)/Al_2O_3$catalysts, after 60 h time-on-stream, the Ti-containing catalyst performs better. This better stability of the Ti-containing catalyst could be related to changes in the adsorption constants of the different poisoning molecules, and/or to an increased hydrogenating activity of the Ti-modified catalyst.

The hydrodenitrogenation results (Fig. 3) follow similar trends to those exhibited for HDS. The catalyst shows greater stability when diesel is used as diluent for either hydrotreated or non-hydrotreated Maya. In fact, the slope of the conversion versus time-on-stream curve is similar for HM-D and M-D. This would indicate that at the scale of time used in this work, the amount of metals deposited on the surface does not affect significantly the activity of the catalyst, and therefore, that the rate of catalyst deactivation observed in both cases, HM-D and M-D, is due to the normal carbon deposition process occurring in all HDT catalysts. Clearly, the drastic deactivation observed when using naphtha as solvent for hydrodemetallized Maya, HM-N, is of a different nature. For this reaction the effect of adding Ti to the catalyst is also beneficial and more pronounced than for HDS.

The HDAs conversion trends (Fig. 4) are also similar to those observed for the HDS and HDN reactions. In this case the Ti-containing catalyst also maintains a higher activity with time-on-stream than the $NiMo/Al_2O_3$ catalyst. Since the active sites for HDS, HDN and HDAs are not the same, it seems unlikely that the abnormal drop in activity observed when using naphtha, is related to the strong adsorption of some component of the naphtha on the active sites of the three different reactions. In fact the competing adsorption species such as sulfur, nitrogen compounds or aromatics are more abundant in diesel and in the untreated Maya. Therefore, it appears that the abnormal drop in the catalyst activity observed when using naphtha as diluent, is due to an unselective process, more related to fouling of the surface than to selective adsorption.

Comparing the activity results of catalysts with and without titanium shows that the titanium-containing catalyst maintains higher activity in the HDS, HDN and HDAs reactions. The higher activity of the titanium-containing catalysts is well in line with previous studies that show enhanced hydrodesulfurization and hydrogenation activities for these catalysts, compared with those supported on pure alumina [9–13]. The incorporation of Ti however did not stop the fast deactivation observed when naphtha was used as solvent for hydrotreated Maya.

The deactivation of hydrotreating catalysts occurs usually by several mechanisms such as, site poisoning by strongly adsorbed species, active site blockage by coke or metal deposits, pore mouth obstruction and active phase sintering. Each of these causes has been widely investigated in the past and has been recently discussed and summarized by [14]. Usually, the main cause of catalyst deactivation is deactivation by coke. In the case of heavy feeds deactivation is mainly caused by asphaltenes, and metal sulfide deposition, which is irreversibly and depends on the metal type and concentration. The formation, crystallization and migration of metal sulfides are considered responsible for pore plugging, attrition and deformation of the catalytic sites in metal-deactivated catalysts. The pore constriction deactivation usually takes place during the final stages of catalyst life and produces a very strong deactivation. The life of the catalyst is then in general dictated by the importance of the first two deactivation mechanisms [15,16], site poisoning by strongly adsorbed species, and active site blockage by coke or metal deposits. In our case, however, these two mechanisms do not seem to be the main cause of the rapid drop in activity observed with naphtha as diluent. As indicated, the carbonaceous deposits are more severe as the feed becomes heavier and in our case the strongest drop in activity for the HDS, HDN and HDAs reactions is observed for the lighter feed. On the other hand, the poisoning by metals should be faster for the heaviest feed, non-hydrotreated Maya-diesel, which according to Table 1 has the highest concentration of metals, and this was not what we observed.

A possible explanation for the abnormally higher drop in activity, observed when using naphtha as diluent, can be found in the solubility behavior of the components of Maya petroleum in naphtha. A work made on the stability of diluted bitumen emulsions reported asphaltene precipitation when bitumen is highly diluted in naphtha. For example, asphaltenes were reported to precipitate in naphtha (N)-bitumen (B) mixtures at 80 °C when the N/B ratio exceeds 4 [17]. It has also been reported that during hydroprocessing of heavy crude, the oil and resin fractions are converted to smaller fragments faster than the asphaltene fraction. Since the asphaltenes are believed to be soluble mainly in the resin fraction, their solubility decreases during conversion of resin. As a result of this, asphaltenes precipitate on the catalyst surface blocking the active surface sites [18]. Therefore it is possible that the change of solvent from diesel to naphtha could bring about the precipitation of asphaltenes. It is known that Maya petroleum has a high concentration of asphaltenes and that these compounds are highly insoluble in *n*-C5 and *n*-C7 hydrocarbons. In fact, the concentration of asphaltenes is normally reported as the amount of compounds insoluble in *n*-C5 or *n*-C7 hydrocarbons.

If the precipitation of asphaltenes is occurring in our case with the naphtha diluent, then a higher concentration of carbon should be detected on the used catalyst, compared with that observed when diesel is used. To obtain some information to support or disprove this idea, the used catalysts were analyzed for total carbon content. The results, shown in Table 3, indicate that indeed a higher carbon concentration exists in the used catalysts exposed to the hydrotreated Maya-naphtha mixture. It appears then that the enhanced deactivation observed with this feed is likely due to asphaltene precipitation.

The HDM reaction does not follow the same behavior than HDS, HDN and HDAs reactions and does not seem to deactivate faster in the presence of naphtha (see Fig. 5). In

Table 3
Carbon and sulfur analysis in used catalysts

Catalyst	After 60 h on-stream		
	Feed	Carbon (wt.%)	Sulfur (wt.%)
NiMo/Al_2O_3	HM-N	16.90	6.53
NiMo/TiO_2(5)/Al_2O_3	HM-N	17.50	7.55
NiMo/TiO_2(5)/Al_2O_3	HM-D	14.94	4.59
NiMo/TiO_2(5)/Al_2O_3	M-D	15.09	6.38

this case a higher initial activity is observed as expected; the catalyst is more active with the lighter feeds. Contrary to the results obtained for the other reactions (HDS, HDN), in this case after 60 h time-on-stream the catalyst appears pretty stable and maintains the same activity trend with the composition of the feed. Nevertheless, for this reaction, the non-hydrotreated Maya feed, which has a higher concentration of metals, nitrogen and sulfur, causes a faster deactivation of the catalyst. In contrast with the other reactions, HDS, HDN, HDAs, for which the incorporation of Ti to the catalyst caused a beneficial effect, for HDM the effect of incorporating Ti to the catalyst was not clearly evident when using HM-N as feed. With this feed the HDM activity of the catalyst remained constant at high levels. It is possible however that with heavier feeds the effect becomes more evident.

The constancy of HDM activity with time on stream when using naphtha as diluent could be related to the possibility of precipitation of asphaltenes due to their low solubility in naphtha. It is known that the Ni and V metals are contained in asphaltenes; therefore the elimination of asphaltenes by precipitation would also cause the elimination of metals. The constancy of the HDM activity then would result from the fact that the elimination of asphaltenes would not be related to the state of the catalytic surface but to a solubility behavior. In other words, the asphaltenes, and hence the metals, would be eliminated in this case by precipitation rather than by catalytic action. Therefore in appearance the catalytic activity remains high and constant with time-on-stream.

The differences in initial activity between HM-N and HM-D, when the precipitation effect has not taken place yet, could be due to changes in the diffusivity of the reacting species caused by the change in solvent. It is well known that large differences in rates of diffusion can be obtained by changing the polarity and/or the molecular weight of the solvent [19].

To explain the higher activity of the titanium-containing catalysts, an attempt was made to determine the number of active sites in the sulfided catalysts by adsorbing NO as probe molecule. The amount of NO adsorbed on the Ti-containing catalyst was 1.25 times higher than for the alumina supported catalyst (see Fig. 6). Since it has been reported that the titania surface can be sulfided under the sulfidation conditions used to activate the catalysts, the NO adsorption of the sulfided support was also evaluated. The results in Fig. 6 show that the support adsorbs a small amount of NO, which is not enough to explain the greater NO adsorption of the Ti-containing catalyst. Therefore, the higher activity of the Ti-containing catalysts seems to be due to the formation of a greater number of vacancies (CUS), believed to be the active sites.

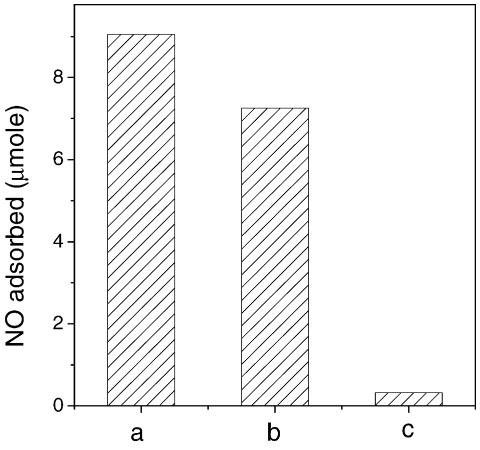

Fig. 6. NO dynamic chemisorption on (a) NiMo/TiO_2(5)Al_2O_3, (b) NiMo/Al_2O_3, (c) TiO_2(5)/Al_2O_3 support.

Information on the behavior of the catalyst can be obtained from selectivity plots in which the different functionalities of the catalyst are referred to one another (Figs. 7–11). When diesel is used as solvent, the selectivity of the catalyst with hydrotreated and non-hydrotreated Maya is oriented more towards HDS than HDN; a greater decrease in the conversion of HDN than HDS is observed. So, the conversion to HDN drops to half while the conversion to HDS only drops about 16% (Fig. 7). The incorporation of Ti to the alumina supported catalyst improves HDN due to an enhancement of the hydrogenating function. It is known that

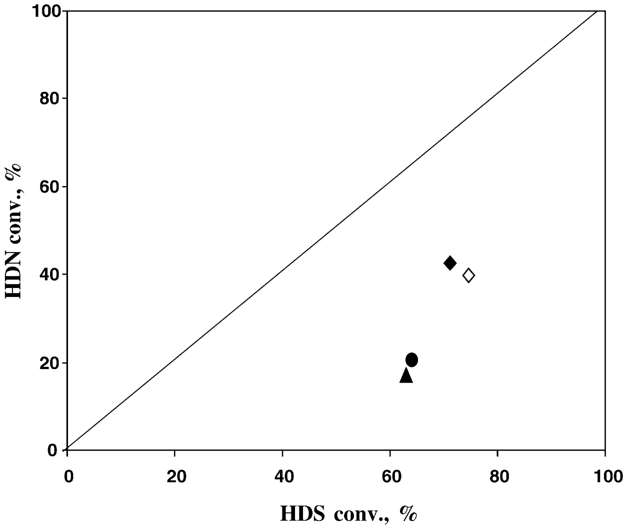

Fig. 7. Selectivity HDN vs. HDS (▲) NiMo/Al_2O_3 with HM-N feed, (◆) NiMo/TiO_2(5)/Al_2O_3 with HM-N feed, (◇) NiMo/TiO_2(5)/Al_2O_3 with HM-D feed, (●) NiMo/TiO_2(5)/Al_2O_3 with M-D feed.

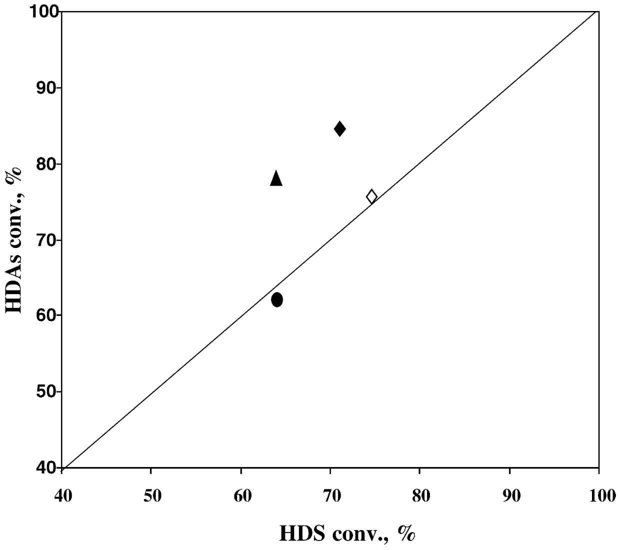

Fig. 8. Selectivity HDAs vs. HDS. (▲) NiMo/Al_2O_3 with HM-N feed, (◆) NiMo/TiO_2(5)/Al_2O_3 with HM-N feed, (◇) NiMo/TiO_2(5)/Al_2O_3 with HM-D feed, (●) NiMo/TiO_2(5)/Al_2O_3 with M-D feed.

to break the C–N bond it is necessary to hydrogenate the ring containing the heteroatom.

Fig. 8 shows that the elimination of asphaltenes is affected similarly to the HDS function when using diesel as solvent. Using naphtha as solvent increases the selectivity towards HDAs due to precipitation caused by their insolubility in naphtha. In this case it is observed that the incorporation of Ti improves the performance of the catalyst possibly due to an enhanced hydrogenating function, which helps to eliminate carbon deposits from the surface.

Fig. 9, where HDM is compared with HDS, indicates that hydrotreating the feed causes a greater increase for HDM than for HDS. This could be related to the fact that pretreatment of the feed eliminates the sulfur compounds which are easily desulfurized and leaves the sulfur compounds with lower reactivity.

A comparison of HDAs versus HDM (Fig. 10), showed a result that was not expected: hydrotreating the feed caused a small increase in the conversion of asphaltenes but an important increase in HDM conversion. The explanation of this result rests on the fact that while the amount of metals was determined by atomic absorption and was highly reliable, the amount of asphaltenes was determined by a solubility test (compounds insoluble in C5). Although many works use the amount of compounds insoluble in C5 to determine asphaltenes, others use the compounds insoluble in C7. It appears from these results that the amount of compounds insoluble in C5 underestimates the amount of asphaltenes almost by half, which is the observed increase in the HDAs/HDM ratio.

Fig. 11 shows that the catalyst used here performs the demetallization of V better than for Ni. This could be related to the greater reactivity of the vanadium species present in the Maya feed. It is known from demetallization studies with model molecules, that vanadil tetra phenyl porphyrin (VO-TPP) is more reactive than Ni tetra phenyl porphyrin (Ni-TPP) [20]. The above results show that the choice of solvent can substantially change the results of the activity tests when processing heavy Maya petroleum.

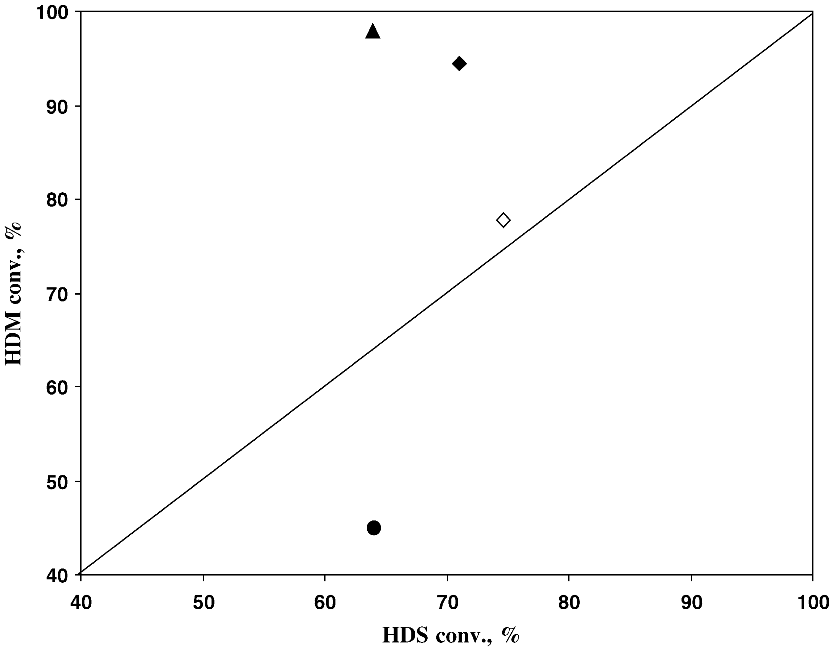

Fig. 9. Selectivity HDM vs. HDS (▲) NiMo/Al_2O_3 with HM-N feed, (◆) NiMo/TiO_2(5)/Al_2O_3 with HM-N feed, (◇) NiMo/TiO_2(5)/Al_2O_3 with HM-D feed, (●) NiMo/TiO_2(5)/Al_2O_3 whit M-D feed.

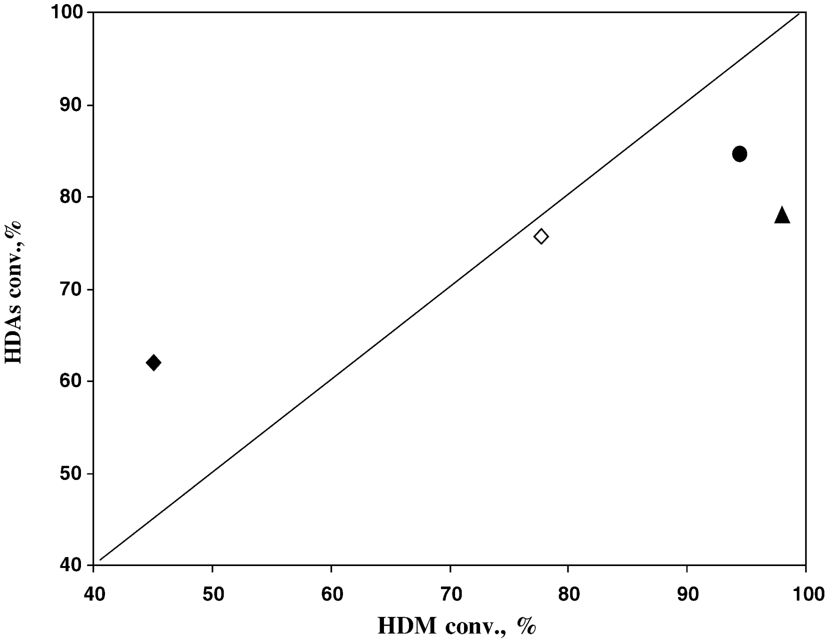

Fig. 10. Selectivity HDAs vs HDM (▲) $NiMo/Al_2O_3$ with HM-N feed, (◆) $NiMo/TiO_2(5)/Al_2O_3$ with HM-N feed, (◇) Catalyst $NiMo/TiO_2(5)/Al_2O_3$ with feed HM-D, (●) Catalyst $NiMo/TiO_2(5)/Al_2O_3$ whit feed M-D.

4. Conclusions

From the above results the following conclusions can be drawn:

1. The choice of diluent when performing catalytic activity tests for the ranking of catalyst formulations for hydrotreatment of heavy petroleum like Maya is critical.
2. The use of naphtha as diluent leads to an increased poisoning of the catalyst surface by carbon deposition originated in part by the insolubility of asphaltenes in the components of naphtha. This effect is not observed when using diesel as diluent. Therefore, it is recommended to use diesel instead of naphtha to dilute the Maya petroleum when trying to avoid, during the catalytic tests, the problems related to the high viscosity of Maya crude.

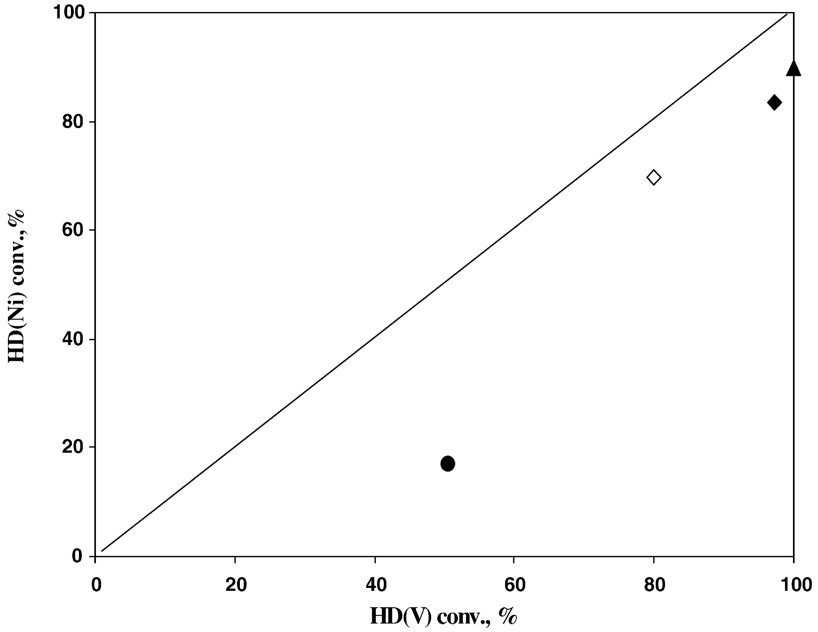

Fig. 11. Selectivity HD(Ni) vs. HD(V). (▲) $NiMo/Al_2O_3$ with HM-N feed, (◆) $NiMo/TiO_2(5)/Al_2O_3$ with HM-N feed, (◇) $NiMo/TiO_2(5)/Al_2O_3$ with HM-D feed, (●) Catalyst $NiMo/TiO_2(5)/Al_2O_3$ with M-D feed.

3. The incorporation of Ti to the support of the conventional NiMo/Al_2O_3 catalyst improves the functionalities of the catalyst (HDS, HDN, HDAs), possibly due to Ti-enhanced hydrogenating and hydrodesulfurization functions. The number of coordinatively unsaturated sites (CUS) on the surface of the sulfided phase was higher in the Ti-containing catalyst.
4. A previous demetallization treatment of the feed increases significantly the performance of the hydrotreatment catalyst in all the reactions HDS, HDN, HDAs and HDM.

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